(54) REACTIVATION OF CARBON DIOXIDE ACCEPTORS

(71) We, CONSOLIDATION COAL COM-
PANY, a corporation organised under the laws
of the State of Delaware, United States of
America, of Koppers Building, Pittsburgh,
5 Pennsylvania, United States of America, do
hereby declare the invention, for which we
pray that a patent may be granted to us, and
the method by which it is to be performed,
to be particularly described in and by the
10 following statement:—

Carbon dioxide (CO_2) is produced as an
undesirable by-product in many processes. In
some of these processes, it is desirable to re-
move the CO_2 as fast as it is formed. For
15 that purpose, solids which readily react with
CO_2 may be used directly in the reaction
zone, provided they do not react with the other
reactants. Such solids are sometimes called
"CO_2 acceptors".

20 When lime (CaO) is used as the CO_2 accep-
tor (and it is the favored acceptor because
of its generally high effectiveness and low
cost), the reaction of CaO and CO_2 to form
$CaCO_3$ which is exothermic will provide the
25 requisite heat, or at least part of it, for endo-
thermic reactions.

A process wherein lime may be used to ad-
vantage as an acceptor for CO_2 involves the
steam-carbon reaction which yields carbon
30 monoxide (CO), methane (CH_4) and hydro-
gen (H_2), as well as the undesired CO_2 as a
by-product. Variants of the process are de-
scribed in many patents.

United States Patent No. 2,705,672 is
35 illustrative. In this process, the heat generated
by the reaction of CO_2 and CaO is nearly
sufficient to supply that required for the endo-
thermic reaction between the steam and
carbon. As described in the cited patent, the
40 regeneration of the calcium oxide is accom-
plished by heating the carbonate to a tem-
perature of about 1700°F. if the pressure in
the regenerator is atmospheric, or at or above
1900°F. if the pressure is at 20 atmospheres
45 or above. The calcium carbonate is thereby
converted to CaO, and the CO_2 evolved is

discharged for other purposes. The lime is
recycled for re-use in the process.

Our experiments have clearly shown that
the lime undergoes progressive decline in its   50
ability to absorb CO_2 despite, or because of,
its repeated cycling through the regeneration
process. The decline in activity may be attri-
buted to growth in crystallite size of the CaO,
with consequent progressive reduction in pore   55
volume on recycling through the steam-carbon
process and associated regeneration step. In
any case, the lime finally reaches the point
where it is essentially inert so far as absorp-
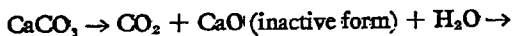tion of CO_2 is concerned.   60

The primary object of the present inven-
tion is to provide a process of making an
active CO_2 acceptor from CaO which has
become inert by frequent uses as above de-
scribed, or which, in its natural state, is not   65
satisfactorily active.

According to the invention, there is provided
a process for regenerating active CaO, wherein
CaO is used to absorb CO_2 to form $CaCO_3$
which is thereafter calcined to regenerate CaO   70
for reuse in absorbing additional CO_2, and
wherein the CaO after repeated cycles of
reuse and regeneration becomes deactivated or
less effective in the absorption of CO_2, which
comprises converting said deactivated CaO to   75
$Ca(OH)_2$, heating a mixture of said $Ca(OH)_2$
and either CaO or $CaCO_3$, or both in the
presence of steam at an elevated pressure which
is sufficiently high to prevent dehydration of
the $Ca(OH)_2$ until the mixture is melted, allow-   80
ing the melted mixture to cool to a solid
state, and calcining the solid to convert the
$Ca(OH)_2$ to CaO, whereby an active CO_2
acceptor is formed.

In the various embodiments of the inven-   85
tion, the CaO is regenerated from the $CaCO_3$
by calcination at an elevated temperature, e.g.
1900°F. As pointed out above, the CaO
is in an inactive state, the extent of inactivity
being dependent upon the number of cycles   90
of carbonation and regeneration it has been
subjected to.

The above process is based on the fact that active CaO may be obtained by reacting the inactive CaO obtained from CaCO$_3$ with water and converting the Ca(OH)$_2$ thus obtained back to CaO. The overall process may be illustrated as follows:

$$CaCO_3 \rightarrow CO_2 + CaO \text{ (inactive form)} + H_2O \rightarrow$$

$$Ca(OH)_2 \rightarrow H_2O + CaO \text{ (active form)}$$

Our invention which involves melting the mixture of Ca(OH)$_2$ and CaO and/or CaCO$_3$, is also based upon the fact that Ca(OH)$_2$ forms low melting eutectic compositions with CaO, or CaCO$_3$, or both, as follows:

1) Ca(OH)$_2$.CaCO$_3$, melting point — 1180°F. The phase diagram for this system is shown in Figure 1.
2) CaO.Ca(OH)$_2$, melting point—1454°F. The phase diagram for this system is shown in Figure 2.
3) CaO.Ca(OH)$_2$.CaCO$_3$.

In order to operate with compositions of the lowest possible melting points, it is obviously desirable to regulate the proportions of the components Ca(OH)$_2$, CaO, and CaCO$_3$ to conform to those of the desired eutectics, although our process as outlined above will still achieve substantial improvements in activity despite substantial deviation from the eutectic proportions.

In accordance with a preferred embodiment of this invention, a mixture of Ca(OH)$_2$ and CaCO$_3$ in approximately 1:1 molar ratio is first obtained. This mixture may be obtained by any one of several procedures, including the following: —

Procedure No. 1: Inactive CaO is converted to Ca(OH)$_2$ by treatment with water (liquid, not vapor) at relatively low temperature, e.g. 300°F. This Ca(OH)$_2$ is then mixed with an approximately equimolar amount of CaCO$_3$ obtained from any source.

Procedure No. 2: Inactive CaO is converted to Ca(OH)$_2$ by treatment with steam in the presence of CaCO$_3$. The molar ratio, of Ca(OH)$_2$ to CaCO$_3$, if not 1:1, may be adjusted by adding CO$_2$.

The mixture of Ca(OH)$_2$ and CaCO$_3$ in 1:1 molar ratio obtained by such procedures is heated to a sufficiently high temperature in the presence of steam to a temperature from 1200°F. to 1350°F. to melt the mixture. The steam pressure in the system is regulated to prevent dehydration of the hydroxide and is generally 9—30 atmospheres.

The molten mixture is allowed to cool, whereby a eutectic solid is formed as shown in Figure 1. The eutectic freezing point is 1180°F. To obtain the eutectic in a finely divided solid state, the molten mixture may simply be allowed to crystallize to a solid mass which is then ground and screened to recover the desired size; or the molten mixture

is allowed to drop through a cooling tower to form uniformly sized particles. The finely divided eutectic is subjected to low temperature dehydration at 1000 to 1100°F. to convert the Ca(OH)$_2$ to CaO, whereby a mixture of CaO and CaCO$_3$ is produced which may then be employed as the CO$_2$ acceptor. As such, it has been found not only to be an active CO$_2$ acceptor, but also to be physically strong so as to withstand many successive regenerations before a repeat of the above-described process of this invention must be resorted to.

It is considered to be within the framework of the process of the present invention to blend various additives with the eutectic melt. Some additives such as various other acidic oxides, carbonates, phosphates, including by way of illustration, P$_2$O$_5$, B$_2$O$_3$, SiO$_2$, Al$_2$O$_3$, Na$_2$CO$_3$, may act as stabilizers to inhibit CaO crystal growth. Other additives may act as catalysts for the reactions in which the CO$_2$ acceptors are used.

A program was carried out to compare the activities of CaO compositions prepared from melts by the process of our invention with the activity of natural limestone.

The charge consisting of Ca(OH)$_2$ and CaCO$_3$ was made up by hydrating CaO in liquid water and mixing with CaCO$_3$ such that the proportion of Ca(OH)$_2$ to CaCO$_3$ was known. The charge was heated in an autoclave to a temperature above the liquidus temperature, usually to about 1350°F. Excess steam pressure was vented.

The system was held at high temperature and pressure, usually 350 p.s.i.g. and 1350°F. for 20 minutes to ensure complete melting and was then cooled at the rate of 5°F. per minute to just below the eutectic temperature and then rapidly to room temperature.

The frozen melt was then crushed and sized to particles of size going through a sieve of 14 × 48 mesh Tyler Standard and calcined to CaO in N$_2$ at 1600°F. in a fluidized bed reactor. The activity was then determined by recarbonation at 1 atmosphere pressure in a fluidized bed at 1500°F. using pure CO$_2$. The activity expressed as fractional conversion of CaO to CaCO$_3$ was determined by weight gain, that is in terms of the carbon dioxide absorbed.

The activities of a number of melts prepared in this way from a natural limestone and from reagent grade materials are com-

pared in Table I below. It is seen that the activities of the melts, as long as they contain 40 mole per cent or more $CaCO_3$, are substantially identical to that obtained from the fresh limestone. A deactivated acceptor was prepared by cycling the fresh limestone 70 times through the calcining and gasification steps of the CO_2 acceptor process described in the previously cited U.S. Patent 2,705,672. The activity of the spent acceptor had dropped to 0.16. The inactive CO was converted to $Ca(OH)_2$ by treatment with hot water at 300°F. for one hour. The resulting mix was then melted and its activity determined by the procedure outlined above with results shown in Table I.

TABLE I

Activity of Melts

Source of $CaCO_3$	Melt Composition Mole %			Activity After Melting
	$CaCO_3$	$Ca(OH)_2$	CaO	
Fresh South Dakota Limestone	47	53		0.62
,, ,, ,, ,,	49	51		0.63
Deactivated Acceptor (Activity 0.16)	17	72	11	0.58
	18	73	9	0.54
C.P. Reagent Chemicals	54	46		0.62
,, ,, ,,	50	50		0.66
,, ,, ,,	43	57		0.62
,, ,, ,,	36	64		0.61
,, ,, ,,	20	80		0.54

The activity of calcined fresh South Dakota Limestone is 0.66

It is seen that the acceptor was substantially completely regenerated, i.e. its activity is essentially indistinguishable from melts prepared from fresh materials of the same composition.

The activity of CO_2 acceptors prepared by our process from South Dakota limestone was compared with that of the raw limestone by continuously recycling through a continuous bench scale unit for carrying out the CO_2 acceptor process described in U.S. Patent No. 2,705,672.

The acceptors were prepared by mixing $Ca(OH)_2$ with raw limestone. The mixture was heated to 1350°F. under 350 psig. steam pressure until it was completely melted. The frozen melt was crushed and sized to obtain a 16 × 28 mesh Tyler Standard acceptor for circulation through the continuous unit. The acceptor thus prepared contained 50 mole per cent $Ca(OH)_2$ and 50 mole per cent $CaCO_3$.

Prior to feeding the frozen melt to the continuous unit, the $Ca(OH)_2$ was converted to CaO by heating at atmospheric pressure and 1000°F.

The raw limestone and the acceptors of this invention were recycled through the regenerator and gasifier vessels of the continuous unit under the conditions shown in Table II. The acceptors prepared by the melt process of this invention are referred to for convenience as melt acceptors.

TABLE II

Conditions for Acceptor Activity Test

Acceptor	16 × 28 Mesh South Dakota Limestone	16 × 28 Mesh Melt Acceptor
Char	35 × 150 mesh devolatilized lignite char	
System Pressure	20 atm.	
Acceptor Circulation Rate (lb./hr.)	5.23	6.53

Gasifier Conditions

Temperature, °F.	1500	
Char Feed Rate (lb./hr.)	1.6	
Char Bed Inventory, lb.	7.8	
Fluidizing Velocity, ft./sec.	0.27	

Outlet Gas Composition, Vol. %

H_2O	20	
H_2	38	
CH_4	5	
CO	10	
CO_2	6	
N_2	21	

Regenerator Conditions

Temperature, °F.	1910	1940
Fluidizing Velocity, ft./sec.	1.1	

Outlet Gas Composition, Vol. %

CO_2	17.5	20
N_2	82.5	80

The operation simulates in all details, a commercial CO_2 acceptor system with the exception that the heat of calcination in the regenerator was supplied electrically instead of by in situ char combustion.

During the operation of the continuous unit, the acceptor enters the gasifier in the fully calcined condition and is recarbonated on falling through the char bed. The driving force for recarbonation, i.e. $Pco_2—(Pco_2)$equil. is 0.5—0.8 atmospheres and the residence time of the acceptor is 7 minutes.

The activity is defined as the ratio moles $CaCO_3$/total moles Ca in the acceptor leaving the gasifier.

The decline in activity of the limestone and of the melt acceptor on recycling a number of times through the system for the two runs of Table II is shown in Figure 3. It is noted that the initial activities of the limestone and the melt acceptor containing 50 mole percent each of $Ca(OH)_2$ and $CaCO_3$ are substantially identical. The melt, how-

ever, declines more rapidly on recycling through the system. It should be noted, however, in Table II that the regenerator temperature was about 30°F. higher in the melt acceptor run and this may be the cause of the more rapid decline in activity.

The higher temperature in the melt acceptor run was not accidental. The regenerator temperature was limited to 1910°F. in the limestone run to prevent agglomeration in the regenerator. The melt acceptor showed less tendency to agglomerate, which permitted an increase in regenerator temperature to 1940°F.

The run also demonstrated one of the other beneficial features of the melt acceptor, i.e. its high physical strength. The attrition rate on passing the acceptor through the process was extremely small, i.e. much less than 0.5 weight per cent/cycle.

A generalized type flowsheet which illustrates how the process may be conducted in practice is shown in Figure 4. The flowsheet is a process for reactivating an acceptor from

the steam-carbon reaction in which carbon monoxide, methane and hydrogen are formed and CO_2 is a by-product and wherein CaO is used to absorb the CO_2 produced and the resulting $CaCO_3$ is calcined to regenerate CaO active CO_2 acceptor. The process is adapted to produce a melt acceptor from either spent coarse acceptor, attrited acceptor fines, recycle fines from crushing and sizing of the melt, fresh limestone and any combination of the above materials.

The flowsheet as shown is illustrated for continuous operation, although the process may be conducted batchwise.

The feed in the feed hopper 10 will contain a mixture of CaO (from either spent acceptor or calcined limestone) and $CaCO_3$. The feed mixture is fed to a melting unit 20 which is a pressurized stirred reactor to which a mixture of steam and CO_2 under pressure at 350—1000 psig. is also fed. The CaO is converted to $Ca(OH)_2$ by reaction with steam while a portion is converted to $CaCO_3$ by reaction with CO_2. The relative amounts of steam and CO_2 reacted are adjusted to give the desired proportions of $Ca(OH)_2$ and $CaCO_3$ in the melt product, i.e. about 50 mole per cent of each.

The exothermic heats of the hydration and carbonation reactions are sufficient to achieve the desired melting temperatures of 1200—1400°F., if the solid charge is preheated to 600—800°F.

The melted acceptor is transferred to a prilling tower 30 through a sprayhead device 32. The molten spray is converted to a steady stream of droplets of approximately the proper size for use in the gasification plant, i.e. between 8 mesh and 28 mesh Tyler Standard. The melted acceptor is cooled and frozen by contact with a gas stream circulated under pressure through the prilling tower from a recirculation system 34. The $Ca(OH)_2$ undergoes partial dehydration, and the endothermic heat of this reaction is sufficient to cause freezing of the melt.

An alternative arrangement is to spray the liquid melt into an immiscible liquid in which a temperature gradient is maintained such that the liquid drops freeze before passing out of the liquid. A possibility here, for example, is to spray the melt upward through a bath of molten lead.

The frozen melt droplets are withdrawn to a hopper 40, and thence to a sieving and crushing system 50. The undersize material from crushing and sizing is returned to the melting unit. The oversize material is crushed. The material of desired size is sent to a calcining unit 60 where the acceptor is calcined at 1000—1200°F. and atmospheric pressure to convert the $Ca(OH)_2$ to CaO before it is sent to the gasification plant.

WHAT WE CLAIM IS:—

1. In a process wherein CaO is used to absorb CO_2 to form $CaCO_3$ which is thereafter calcined to regenerate CaO for re-use in the process, and wherein the CaO after repeated re-use becomes deactivated or less effective in the absorption of CO_2, the improvement for restoring said deactivated CaO to an effective CO_2 acceptor, which comprises the following steps: (a) converting said deactivated CaO to $Ca(OH)_2$, (b) heating a mixture of said $Ca(OH)_2$ and either CaO or $CaCO_3$ or both in the presence of steam at an elevated pressure which is sufficiently high to prevent dehydration of the $Ca(OH)_2$ until the mixture is melted, (c) allowing the melted mixture to cool to a solid state, and (d) calcining the solid from step (c) to convert the $Ca(OH)_2$ to CaO, whereby an active CO_2 acceptor is formed.

2. A process according to Claim 1 in which the inert CaO is converted in step (a) by treatment with liquid water.

3. A process according to Claim 1 in which the mixture of step (b) is a mixture of $Ca(OH)_2$ and $CaCO_3$ in approximately 1:1 molar ratio.

4. A process according to Claims 1, 2 or 3 in which the CO_2 is formed as a by-product when steam is reacted with carbon to form CO, CH_4 and H_2.

5. In the reaction of steam with carbon in which carbon monoxide, methane and hydrogen are formed and CO_2 is a by-product and wherein CaO is used to absorb the CO_2 produced and the resulting $CaCO_3$ is calcined to regenerate CaO active CO_2 acceptor, the improvement in the regeneration of the CaO active CO_2-acceptor, which comprises the following steps: (a) introducing a mixture of deactivated CaO and $CaCO_3$ into a pressurized stirred reactor, (b) feeding a mixture of steam and CO_2 to said stirred reactor while maintaining the pressure therein between 350 and 1000 psig and the temperature between 1200—1400°F. whereby part of the CaO is converted to $Ca(OH)_2$ by reaction with the steam, and part is converted to $CaCO_3$ by reaction with CO_2, the relative amounts of steam and CO_2 reacted being adjusted to yield a molten product containing about 50 mole percent of $Ca(OH)_2$ and 50 mole percent of $CaCO_3$, (c) cooling the molten product from step (b) to a solid state, and (d) calcining the solid product to convert $Ca(OH)_2$ to CaO.

6. A process according to Claim 5 wherein the molten product from step (b) is passed through a prilling tower to form solid droplets.

7. A process for regenerating CaO in the active form as CO_2-acceptor, from deactivated CaO, essentially as hereinbefore described and illustrated in the accompanying drawings.

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FIG.1

PHASE DIAGRAM FOR THE SYSTEM
Ca CO₃ — Ca(OH)₂

FIG. 2

PHASE DIAGRAM FOR THE SYSTEM
CaO — Ca(OH)₂

FIG. 3

RATE OF ACTIVITY DECLINE

SOUTH DAKOTA LIMESTONE

MELT ACCEPTOR — { 50% $Ca(OH)_2$
50% $CaCO_3$

ACTIVITY

NO. OF CYCLES

FIG.4

CALCINED LIMESTONE
OR SPENT ACCEPTOR

MAKE UP LIMESTONE

FEED HOPPER Ca 800°F

FINES RECYCLE

~10

INERT BLEED OFF

STEAM

~20

WATER IN

MELTING UNIT

CO₂ IN

32

"PRILLING" TOWER

30

WATER OUT

34

INERT GAS RECYCLE

WITHDRAWAL HOPPER

40

SIEVING

CRUSHING

50

FINES RECYCLE TO MELTING UNIT

CALCINING   60

REACTIVATED ACCEPTOR TO GASIFICATION PLANT